SERI/PR-8104-2-T1
Distribution Category UC-63e

# COMMERCIALIZATION OF A THICK FILM SOLAR CELL

QUARTERLY TECHNICAL PROGRESS REPORT

April 1, 1980 TO June 30, 1980

BY

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SUBCONTRACT NO. XS-9-8104-2
PRIME CONTRACT NO. EG-77-C-01-4042

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Abstract

Samples of screen printed cadmium sulfide were supplied to the Institute of Energy Conversion of the University of Delaware for the application of copper sulfide via the evaporated cuprous chloride technique. Results of this activity are not available at this time.

Problems were encountered in reproducing the previously obtained low resistivity cadmium sulfide films. The probable cause of this problem is in the atmosphere control for the furnace. The furnace has been extensively modified. When completed the modifications will permit greater control over the atmosphere, flow rate, and composition.

A trial solar cell was prepared. While its short circuit current and open circuit voltage are low, present procedures for applying the cuprous chloride appear adequate. An attempt was made to apply the cuprous sulfide layer via a screen printed, fired-on copper electrode. The resultant copper electrode lacked adhesion to the cadmium sulfide layer.

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## 1. Introduction

This report is the third quarterly report of a program designed to evaluate the use of screen printing as a technique for producing large area solar cells. The attributes of screen printing which make this approach of interest are that it is a well established technique in the electronics industry with well established requirements; it has a demonstrated ability to produce large areas of electronic quality films with good pattern fidelity; it affords means for separating conditions required for film deposition from those required for sintering, which permits better control over microstructure; and it is characterized by high material utilization efficiency. A possible disadvantage of screen printing is that the starting material must be reduced to a powder. The fact that efficient small area solar cells can be prepared by screen printing is documented in the current literature. (1)

In previous quarterly reports the comminution of cadmium sulfide and cadmium telluride and the preparation of the first trial films of these materials has been reported. This report covers the improvement made in the preparation of these films and the initial attempt to produce a complete solar cell. Delays were encountered during this quarter due to modification of the kiln used to fire the films. This modification when completed will permit continuous variation of the oxygen partial pressure of the firing atmosphere from that of pure oxygen through that of humidified nitrogen to that of pure nitrogen.

## 2. Experimental

### 2.1. Materials

The sources, purity, and preliminary processing of the materials used have been described in the previous quarterly reports. The following additional materials have been employed:

Cuprous chloride was obtained from Alfa Products. TPA-85, a masking material, was obtained from American Liquid Xtal Chemical Corporation. The TPA-85 as received was found to be unsatisfactory. Entrained air bubbles formed during screen printing this material through a 325 mesh screen failed to be liberated before final film curing. This resulted in pin holes in the final product. The addition of 2-ethoxyethyl ether (diethyl "Carbitol") from Aldrich Chemical Company lowered the viscosity of the TPA-85 and resolved this problem.

A low temperature copper metallization ink, 7029-5, was obtained from Cermalloy Inc.

### 2.2. Equipment

The equipment described below augments the equipment described in the previous quarterly reports.

A Tempress 500 cubic feet per hour atmosphere saturation bottle (controlled atmosphere humidifier) was installed on the belt furnace. This device will permit, when fully operational, the use of the following atmospheres in the furnace: air, nitrogen, humidified nitrogen, and hydrogen-nitrogen mixtures. Full installation of this equipment is not complete at this time. Photographs of this equipment are shown in Figures 1 and 2.

A research photo detector, IL510A manufactured by International Light, Inc. was obtained to monitor the light intensity of the Schaeffel Universal one kilowatt Short-Arc Solar Simulator.

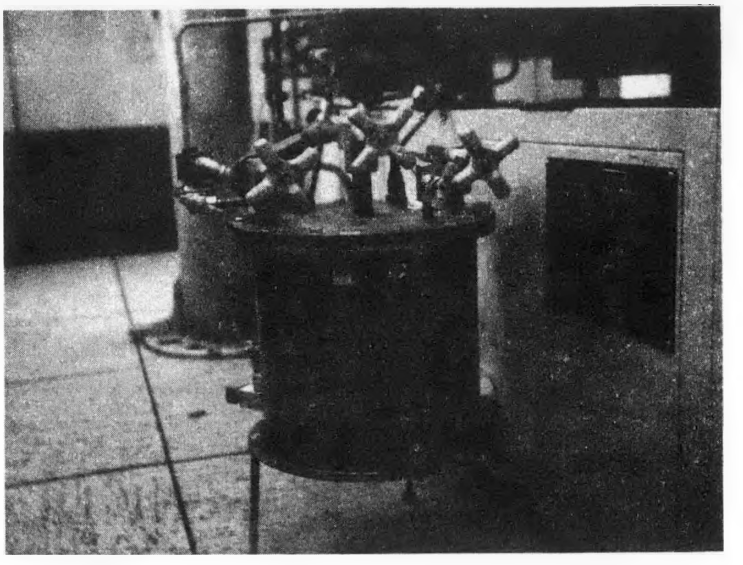


Figure 1. Front view of gas humidifier.

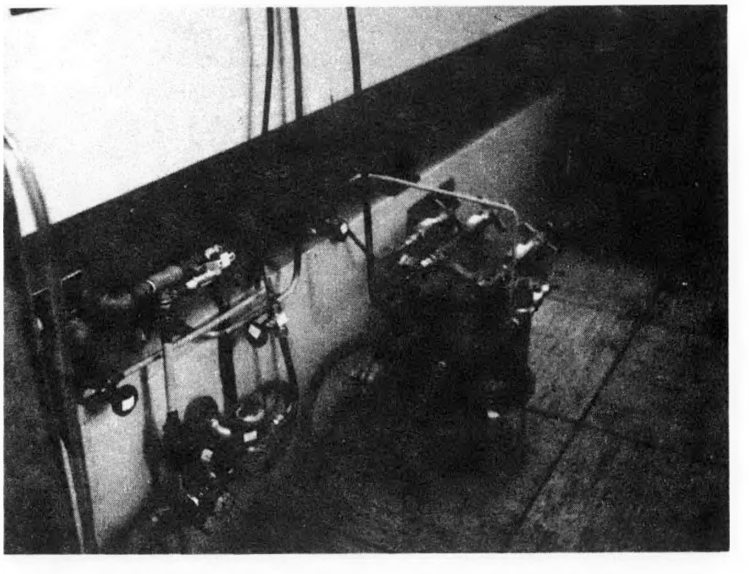


Figure 2. Back view of gas humidifier.

## 3. Technical Discussion

### 3.1. Preparation of Cadmium Sulfide Films for IEC

At the request of D. W. Haines of SERI cadmium sulfide films were prepared for junction formation via cuprous sulfide evaporation at the Institute for Energy Conversion of the University of Delaware. New screen masks were prepared to print the layer 2 cm by 2 cm pattern. Cadmium sulfide films were screen printed on 0.048 inch thick Nesation glass substrates. The screen printing ink consisted of forty weight percent vehicle which in turn contained twenty-five weight AB (Acryloid B67), 37.5 weight percent BCA (butyl "Carbitol" acetate), and 37.5 weight percent AT (α-terpineol). The remaining sixty weight percent was solids consisting of forty volume percent cadmium chloride and sixty volume percent cadmium sulfide. The printed films were fired at 630°C in nitrogen for 35 minutes. Figures 3 through 6 are SEM photographs of the film produced. Resistivity measured using probes on the cadmium sulfide was approximately five ohm-cm. Results of the application of cuprous chloride via vacuum evaporation by IEC are not known at this time. Phosphorescence spectra of the CdS films failed to correspond to either the "green" or "red" spectra seen by IEC on their sputtered material.

### 3.2. Reproducibility of Cadmium Sulfide Film Preparation

A study was initiated to determine the optimum firing conditions for preparing cadmium sulfide films. Films were fired between 600 and 720°C for times varying between 35 and 95 minutes. The resistivities of these films were between 3,000 and 10,000 ohm cm. In addition to the three orders of magnitude, increase in resistivity over those previously produced, the films were generally photoresistive (resistance increasing by approximately an order of magnitude on exposure to room lights) whereas previous films had shown a slight photoconductivity. Three possible causes of this change in performance were suspected: contamination from other materials fired in the furnace, use of a new batch of glass substrates of changed composition, and a change in ambient humidity.

The cross contamination possibility is unlikely since the quantity of copper metallization fired in the furnace was small and the furnace was subsequently purged with air at 1000°C for 48 hours, without improvement in the films. Analysis of the CdS films failed to detect any contamination.

Analysis of the glass substrates did show appreciable change in the glass received in the last shipment, see Figures 7 and 8. However, samples printed on the old glass substrates behaved similarly to the films produced on the new glass.

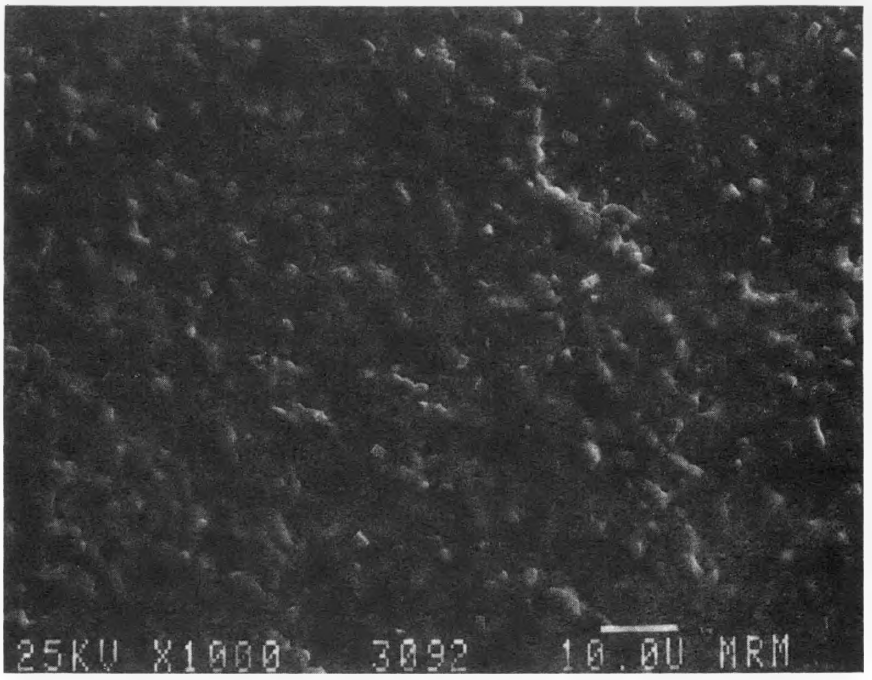



Figure 3. Surface of cadmium sulfide film at low magnification.


Figure 4. Surface of cadmium sulfide film at high magnification.

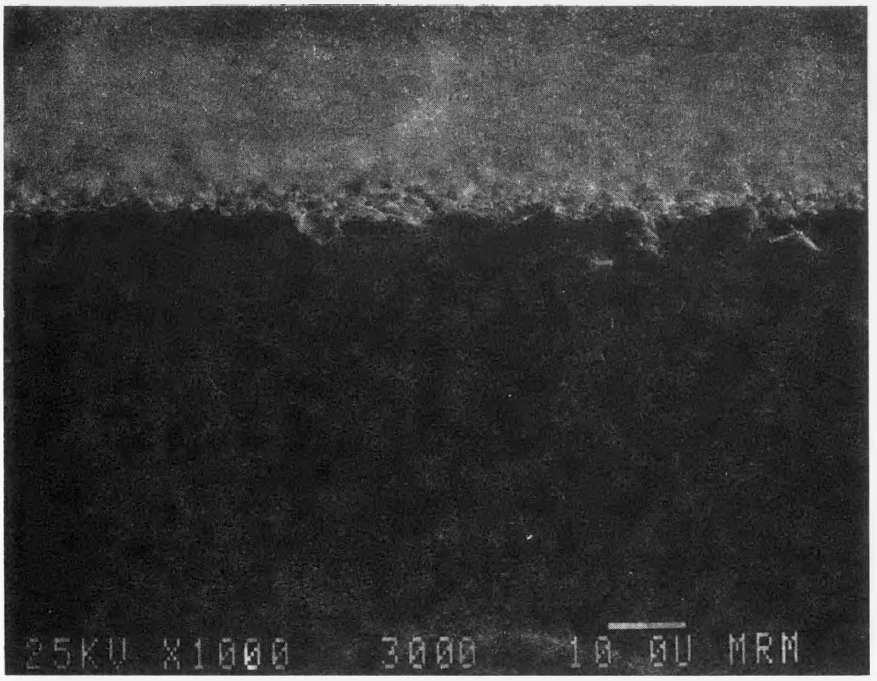



Figure 5. Cross section of cadmium sulfide film at low magnification.

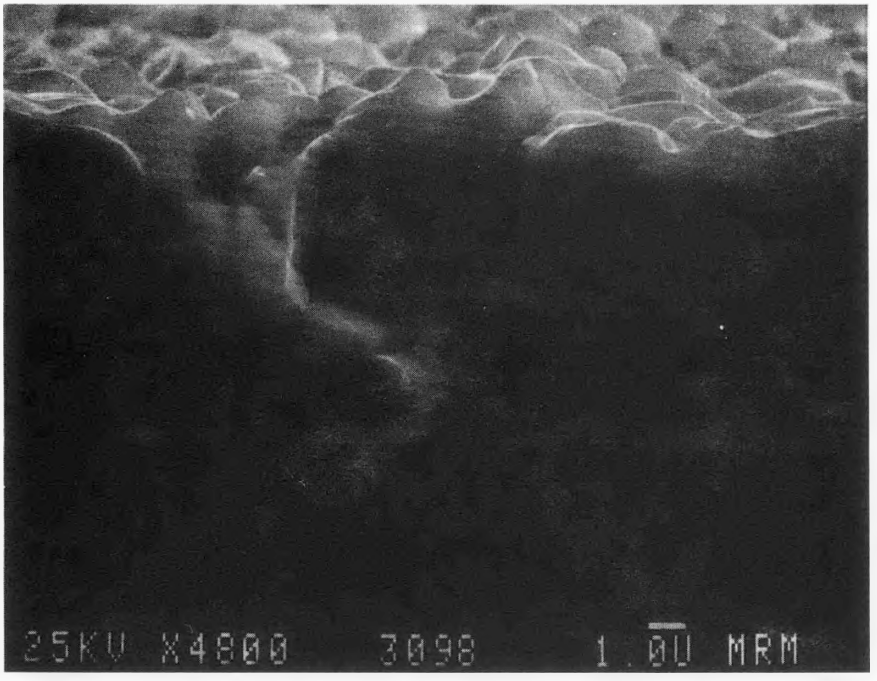



Figure 6. Cross section of cadmium sulfide film at high magnification.

◆ ◆ ◆ G L O B E  U N I O N ◆ ◆ ◆

◆◆◆ MATERIALS TEST LABORATORY SPECTROGRAPHIC REPORT ◆◆◆
CORP. ADDRESS 1XE DATE 05/09/80
PHONE 2366

PHOTO PLATE # 1833.34

MTL # 8005-6003 EXPOSURE 7 T&R SHEET # 80-5/2

| ELEMENT | CONCENTRATION IN % BY WT OF SAMPLE AS RECEIVED BY MTL |
|---|---|
| 13 ALUMINUM | > 1.500 |
| 51 ANTIMONY | .247 |
| 33 ARSENIC | 1.248 |
| 56 BARIUM | > 1.000 |
| 83 BISMUTH | < .010 |
| 48 CADMIUM | < .030 |
| 20 CALCIUM | < .050 |
| 24 CHROMIUM | < .003 |
| 27 COBALT | < .005 |
| 29 COPPER | < .002 |
| 79 GOLD | < .010 |
| 1 HITIN | .601 |
| 26 IRON | .025 |
| 50 LOTIN | .475 |
| 25 MANGANESE | < .0010 |
| 12 MAGNESIUM | .144 |
| 80 MERCURY | < .100 |
| 28 NICKEL | < .003 |
| 78 PLATINUM | < .033 |
| 14 SILICON | > 1.000 |
| 47 SILVER | < .0010 |
| 11 SODIUM | .179 |
| 22 TITANIUM | < .010 |
| 23 VANADIUM | < .003 |
| 40 ZIRCONIUM | .064 |
| 30 ZINC | < .050 |

CUST. IDENT. ◆◆◆◆◆ #1 7059 Corning glass .048" thick

THE ACCURACY OF THESE RESULTS AT THE 95% CONFIDENCE LIMIT IS APPROXIMATELY + OR - 50% OF THE AMOUNT PRESENT AT THE .01% LEVEL. THE ACCURACY DECREASES SUBSTANTIALLY AS THE ELEMENT CONCENTRATION APPROACHES THE CURRENT SPECTROGRAPHIC DETECTION LIMIT.

THIS ANALYSIS HAS BEEN CORRECTED FOR ANY CONTAMINATION INTRODUCED BY THE REAGENTS USED IN THE SAMPLE PREPARATION. THIS INFORMATION IS AVAILABLE UPON REQUEST.

Figure 7. New Lot of 7059 Corning Glass

◆ ◆ ◆ G L O B E  U N I O N ◆ ◆ ◆

◆◆◆ MATERIALS TEST LABORATORY SPECTROGRAPHIC REPORT ◆◆◆
CORP. ADDRESS 1XE DATE 05/09/80
PHONE 2366

PHOTO PLATE # 1833.34

MTL # 8005-204 EXPOSURE 9 T&R SHEET # 8-5/2

ELEMENT CONCENTRATION
IN % BY WT OF SAMPLE AS RECEIVED BY MTL

CUST. IDENT. ◆◆◆◆◆ #2 7059 corning glass .048" thick

| | | |
|---|---|---|
| 13 ALUMINUM | > | 1.500 |
| 51 ANTIMONY | < | .010 |
| 33 ARSENIC | | .463 |
| 56 BARIUM | > | 1.000 |
| 83 BISMUTH | < | .010 |
| 48 CADMIUM | < | .030 |
| 20 CALCIUM | < | .050 |
| 24 CHROMIUM | < | .003 |
| 27 COBALT | < | .005 |
| 29 COPPER | < | .002 |
| 79 GOLD | < | .010 |
| 1 HITIN | | .085 |
| 26 IRON | | .029 |
| 50 LOTIN | | .034 |
| 25 MANGANESE | < | .0010 |
| 12 MAGNESIUM | | .013 |
| 80 MERCURY | < | .100 |
| 28 NICKEL | < | .003 |
| 78 PLATINUM | < | .033 |
| 14 SILICON | > | 1.000 |
| 47 SILVER | < | .0010 |
| 11 SODIUM | < | .050 |
| 22 TITANIUM | < | .010 |
| 23 VANADIUM | < | .003 |
| 40 ZIRCONIUM | | .052 |
| 30 ZINC | < | .050 |

THE ACCURACY OF THESE RESULTS AT THE 95% CONFIDENCE LIMIT IS APPROXIMATELY + OR - 50% OF THE AMOUNT PRESENT AT THE .01% LEVEL. THE ACCURACY DECREASES SUBSTANTIALLY AS THE ELEMENT CONCENTRATION APPROACHES THE CURRENT SPECTROGRAPHIC DETECTION LIMIT.

THIS ANALYSIS HAS BEEN CORRECTED FOR ANY CONTAMINATION INTRODUCED BY THE REAGENTS USED IN THE SAMPLE PREPARATION. THIS INFORMATION IS AVAILABLE UPON REQUEST.

Figure 8. Old Lot of 7059 Corning Glass

Finally, an alteration of the screened film by ambient humidity was ruled out by firing samples which had been previously printed under less humid conditions and stored in a desiccator. The current films were highly resistive compared with the former films which had had resistivities of approximately 10 ohm cm.

When the nitrogen flow rate to the furnace was increased, the films were extremely resistive (100 megohms) and lacked adhesion to the substrate.

At this time it was noted that two furnace baffles which had been accidently knocked out had been replaced by the maintenance department. On the premise that the poor results may have been related to the absence of air back-diffusing into the furnace, a firing was performed at a lower nitrogen flow rate. It was noted that the middle samples had a gray coloration while the first and last samples were not discolored. On the further premise that the discoloration was due to incomplete removal of the binder and/or flux ($CdCl_2$) in the low nitrogen flow, the samples were spaced farther apart on the belt, six inches apart. Only the middle samples showed any discoloration and the properties of the other films were restored to those originally obtained (low resistivities and a slight photo conductivity).

The low nitrogen flow rate, one cubic foot per hour to the end zones and three cubic feet per hour to the center zone was found to be difficult to control. A gas humidifier and mixer was installed on the furnace by Tempress. The presence of numerous leaks (air, nitrogen, hydrogen, and water), wiring which did not conform to local electrical codes, the presence of faulty equipment (leaking air solenoid, plugged mixer chamber, defective nitrogen regulator, and intermittent electrical overloads), and the absence of any part identification or updated blue prints resulted in considerable delay. At the present time most of the trouble areas have been circumvented but final resolution of the problems will not be accomplished until next month.

### 3.3. Sintering of Cadmium Sulfide in Hydrogen Sulfide

The grain size of the cadmium sulfide in the fired films will be studied as a function of post-firing thermal treatment in hydrogen sulfide. Equipment has been assembled and is ready for handling the hydrogen sulfide. Actual treatment of samples has been delayed so that suitable samples can be prepared after the furnace modifications are complete.

## 3.4. Junction Formation in Cadmium Sulfide

An investigation was started to determine the conditions for the formation of an optimum curpous sulfide layer on a cadmium sulfide film. Initially, no purification of the starting materials was employed. A saturated solution of cuprous chloride in one normal HCl was heated to 70°C. An argon atmosphere was maintained over the solution by continuously bubbling argon through this solution.

A cadmium sulfide film (three layer film) was a relatively high resistivity (260 ohm-cm) was used as a trial film. The two cm by one cm CdS pattern with the four probe silver electrodes was masked with a plastic film of TPA 85 (American Liquid Crystal Co.) so that only a 0.8 cm by 0.8 cm. area of CdS remained exposed. This film was then dipped into the hot $Cu_2Cl_2$ solution for six seconds. It was attempted to use the transparency of the film as a measure of the copper treatment. The light transmission through the film before and after this treatment is shown in Figure 9. However, the apparent lack of sensitivity of the laser probe limits its use as a means of following the development of the cuprous sulfide layer. The sample was washed in distilled water and isopropyl alcohol. It was then dried in a vacuum desiccator overnight. A 0.8 cm by 0.8 cm silver electrode was screen printed over the cuprous sulfide layer and air dried. The sequence of layers deposited is shown graphically in Figure 10 and a photograph of the completed cell is shown in Figure 11. In this first sample no attempts were made to optimize any of the cell parameters.

## 3.5. Device Testing

The current-potential performance of the first trial CdS-$Cu_xS$ solar cell is shown in Figure 12. The three curves shown were taken simultaneously from right to left. Each curve contains five hundred data points taken at 45 msec time intervals. The temperature and light intensity curves are included to monitor these variables during the measurement of the J-V characteristics. The low $J_{sc}$ (0.86 ma/cm$^2$) and low $V_{oc}$ (0.3 volts) are not surprising in view of the absence of any optimization.

## 3.6. Formation of Cadmium Telluride Films on Cadmium Sulfide

Initial work indicated that CdTe films can be prepared on glass substrates using conditions similar to those for CdS. An attempt was made to co-fire CdTe and CdS films. Three layers of CdS were prepared on a 7059 glass substrate using an ink containing 40 weight percent V25-5 vehicle; which contains 25 weight percent AB (Acryloid B67), 37.5 weight percent BCA (butyl "Carbitol" acetate) and 37.5 weight percent AT (α-terpineol); and 60 weight percent of a mixture containing 40 volume percent $CdCl_2$ and the remainder CdS. One layer of

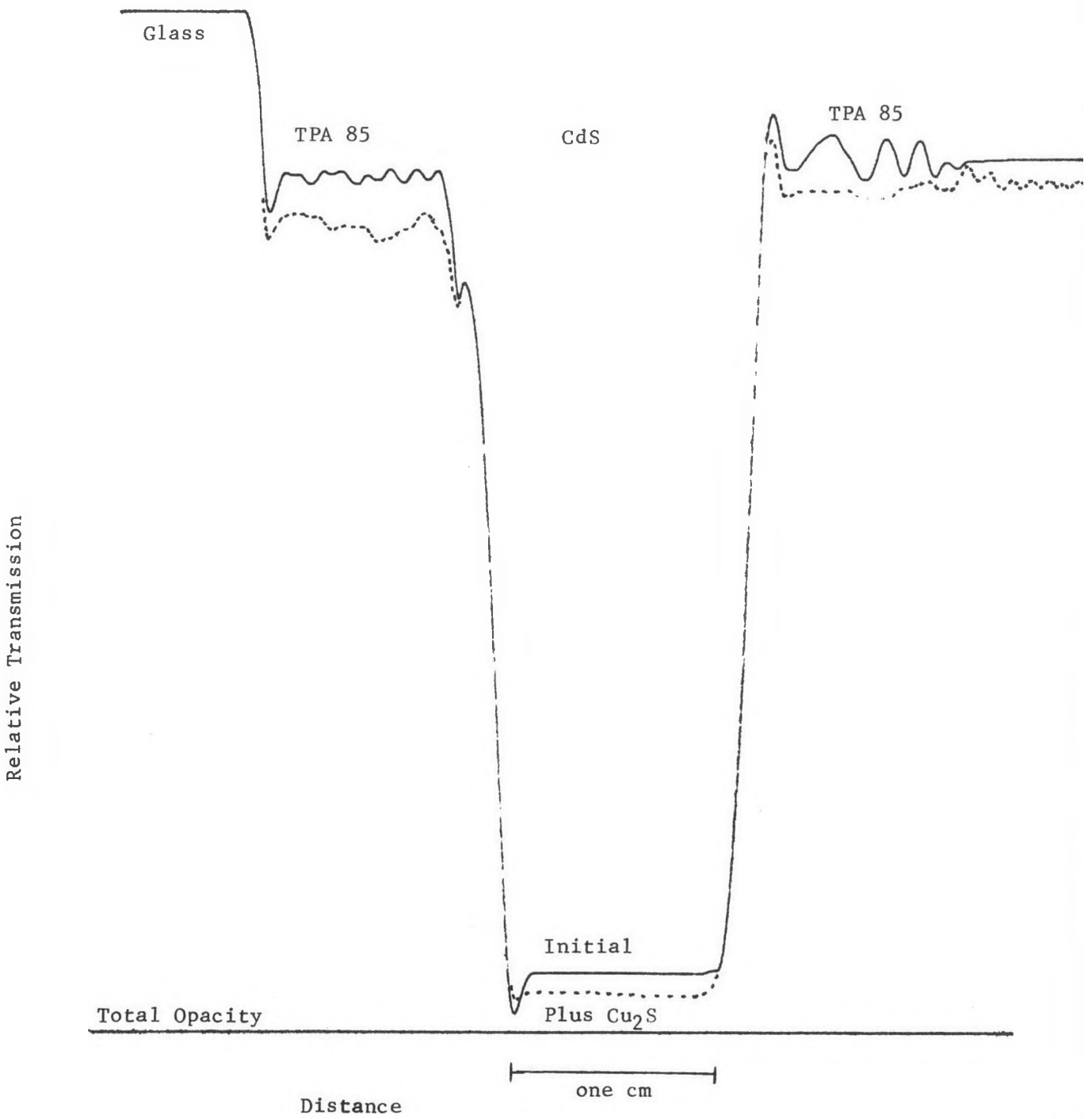



Figure 9. Laser Probe Analysis of CdS Film

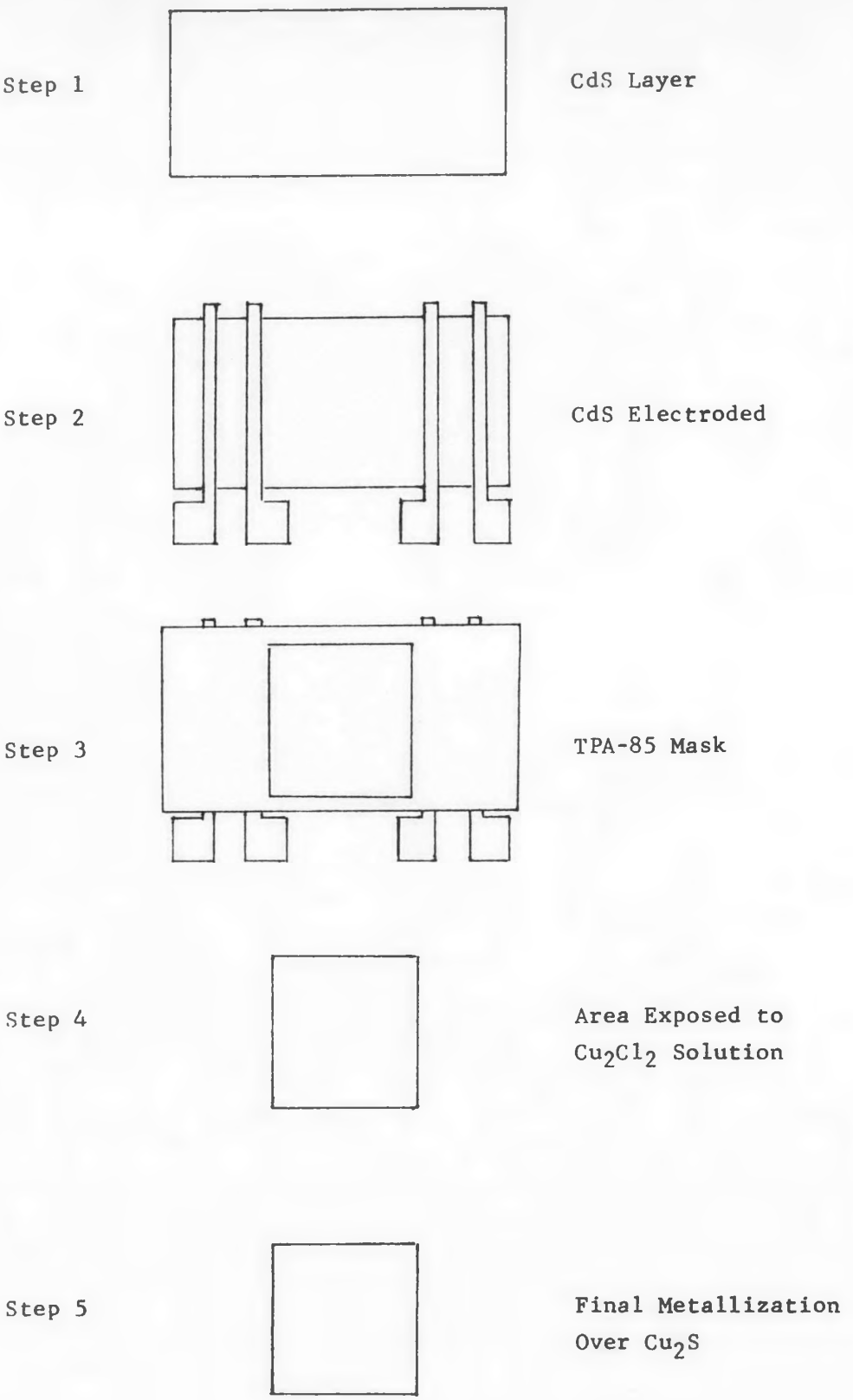



Figure 10. Steps Used to Form CdS Solar Cell

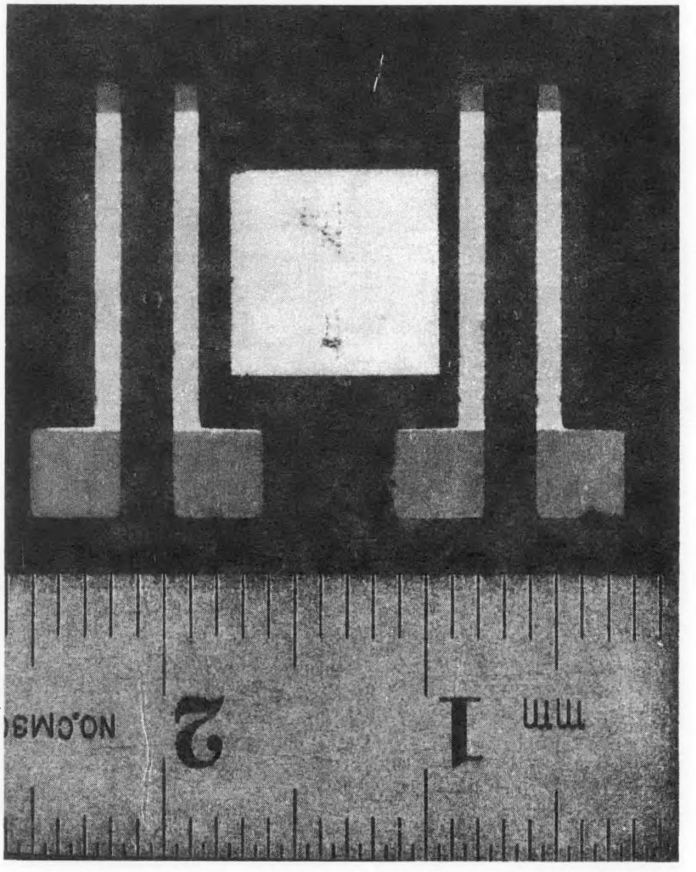
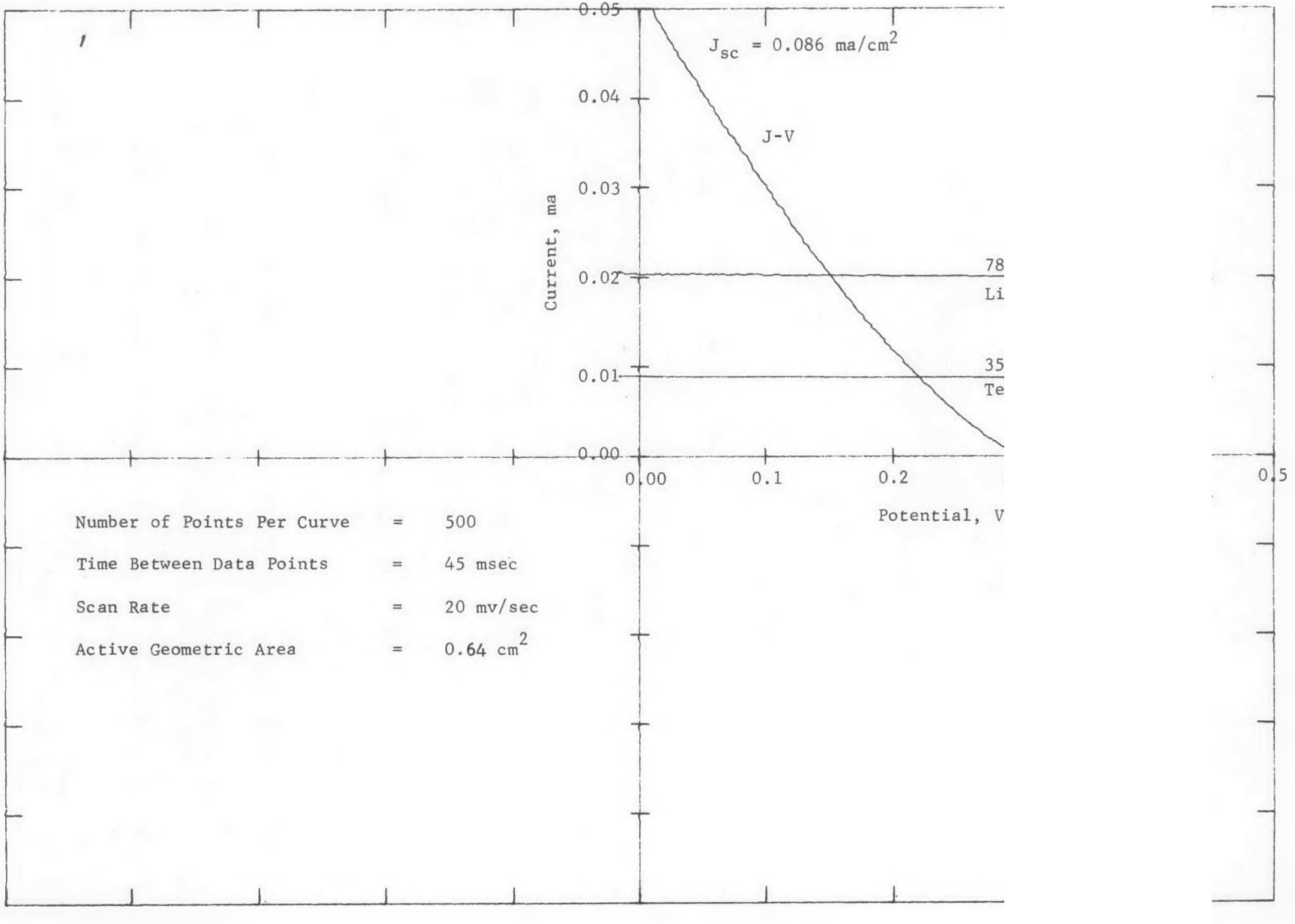


Figure 11. Trial CdS-$Cu_xS$ cell.

Figure 12. Current-potential Performance of Trial CdS-$Cu_xS$ Solar Cel



CdTe was printed over the three layers of CdS using an ink of similar composition as the CdS ink except with CdTe replacing the CdS. This film was fired at 620°C for 45 minutes. The resulting film was gray when viewed from the top or through the glass substrate indicating complete interdiffusion of the layers.

Attempts were then made to apply CdTe layers onto prefired CdS films. When multiple layers of CdTe were fired onto the CdS layer interdiffusion was again encountered. A single layer of CdTe was then printed over the CdS film and on another sample a CdTe layer without any $CdCl_2$ was fired onto the CdS film. Figures 13 through 16 indicate S.E.M. and probe work performed on the latter two films.

Figures 13 and 14 are fracture cross sections of the fluxed ($CdCl_2$-containing) CdTe-CdS layers. The density of the CdS layer was not as great as previously obtained reflecting some of the firing problems described earlier in this report. Figure 15 shows the area of the CdTe-CdS film corresponding to the tellurium map shown in Figure 16. The CdTe layer appears to be well sintered and adherent. Minimal interpenetration of the CdTe and CdS layers can be seen.

Figures 17 and 18 are S.E.M. photographs of the unfluxed CdTe film (note that the glass substrate is on the left side in these photographs while previously it was on the right side). The CdTe layer is not well sintered and little grain growth is noted. A sulfur map shown in Figure 19 and a sulfur scan shown in Figure 21 indicate essentially no sulfur penetration into the CdTe.

The tellurium map shown in Figure 20 and the tellurium scan shown in Figure 22 show that tellurium has penetrated to the glass substrate. While this penetration will probably have no deleterious effect on the electrical performance of a cell prepared from this film the presence of an isolated CdTe layer at the glass-CdS interface may absorb some of the incident light entering the cell.

## 3.7. Copper Metallization

An attempt was made to form the cuprous sulfide layer and the near electrical contact in one step using a low temperature screen printed copper electrode. A cadmium sufide pattern was printed onto a 7059 glass substrate using the screen pattern shown in step 1 of Figure 10. This film was fired in the usual fashion (45 minutes at 630°C under nitrogen). The Cermalloy copper metallization was then overprinted using the screen pattern shown in step 5 of Figure 10. This layer was fired at 625°C for six minutes under a nitrogen atmosphere in the belt furnace. Silver electrodes were then screened on using the patterns shown in step 2 and step 5 of Figure 10.

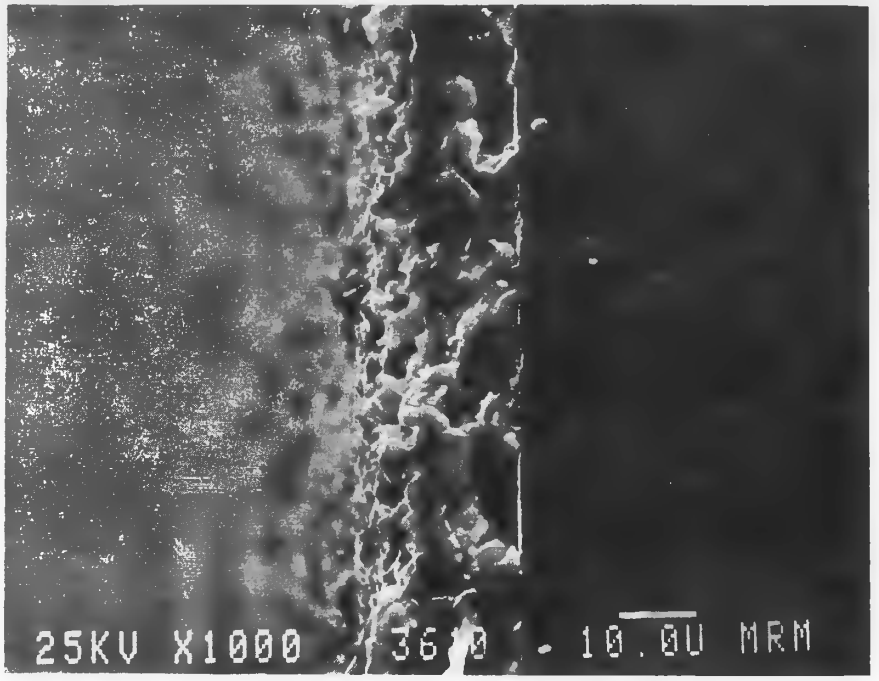



Figure 13. Low magnification of fluxed CdTe layer on CdS.

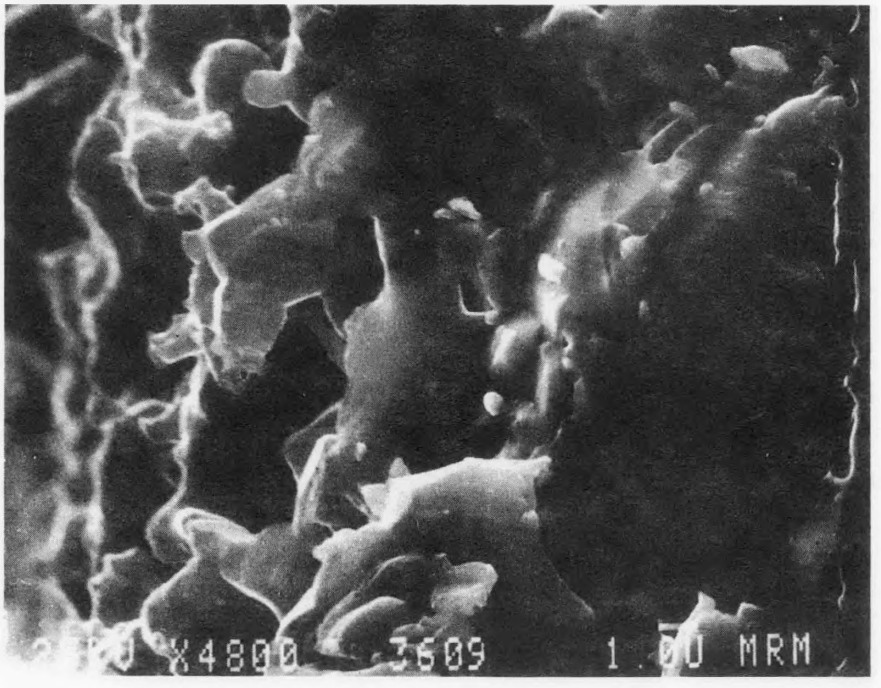



Figure 14. Higher magnification of fluxed CdTe layer on CdS.

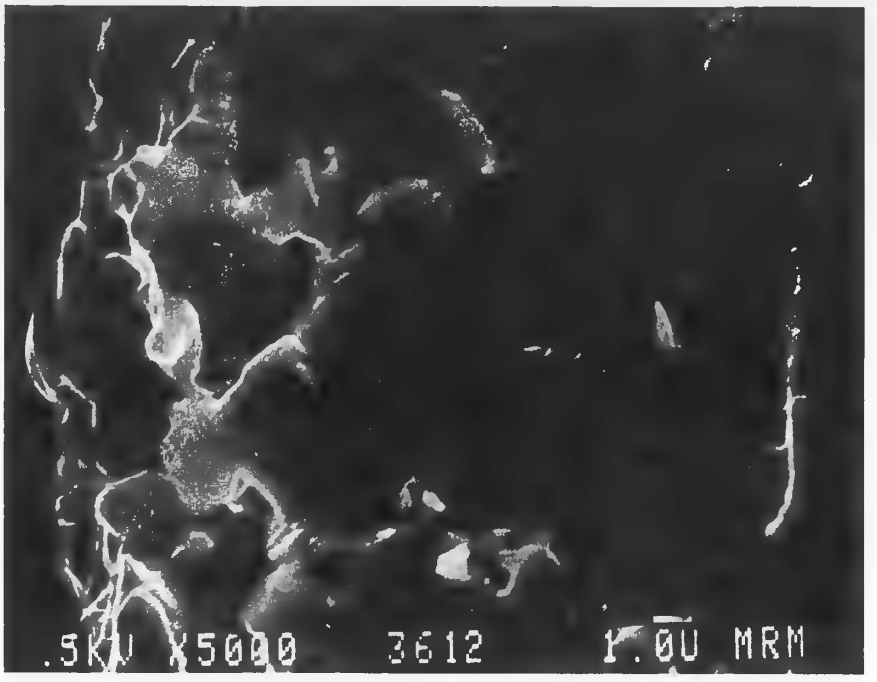



Figure 15. Area mapped for Te on fluxed CdTe layer on CdS.

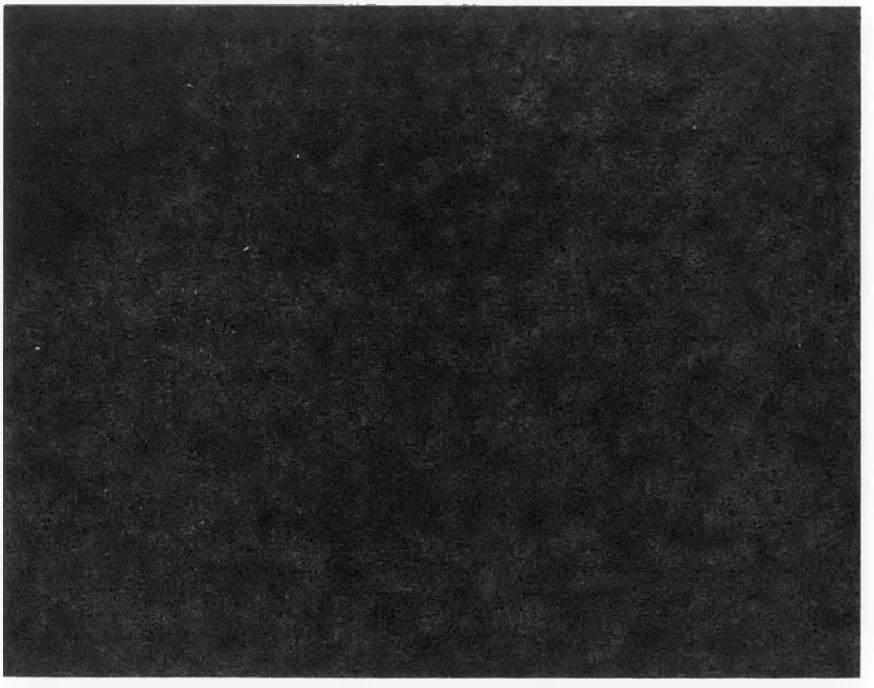


Figure 16. Tellurium map of fluxed CdTe layer on CdS.

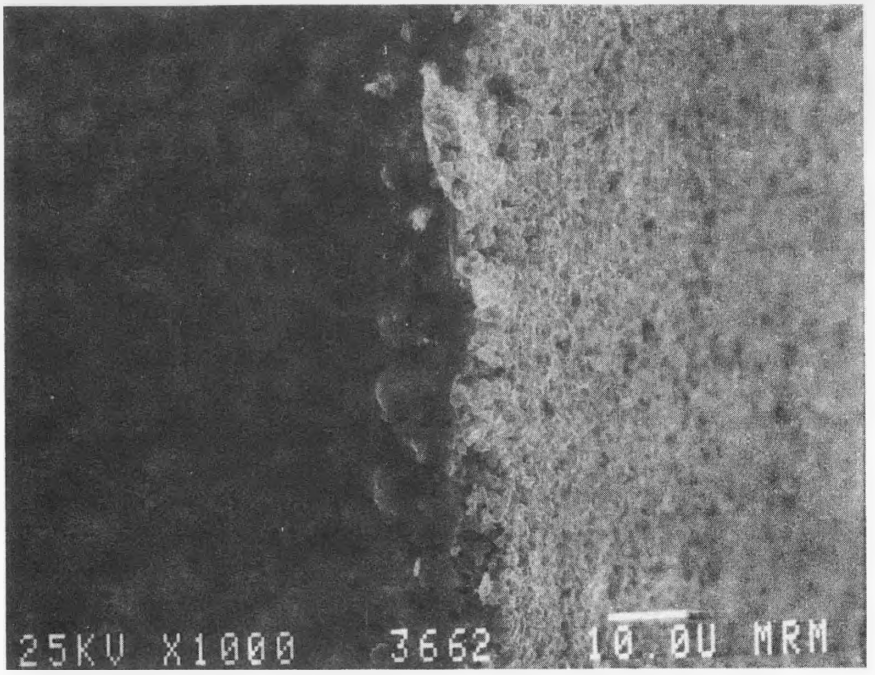



Figure 17. Low magnification of unfluxed CdTe layer on CdS.

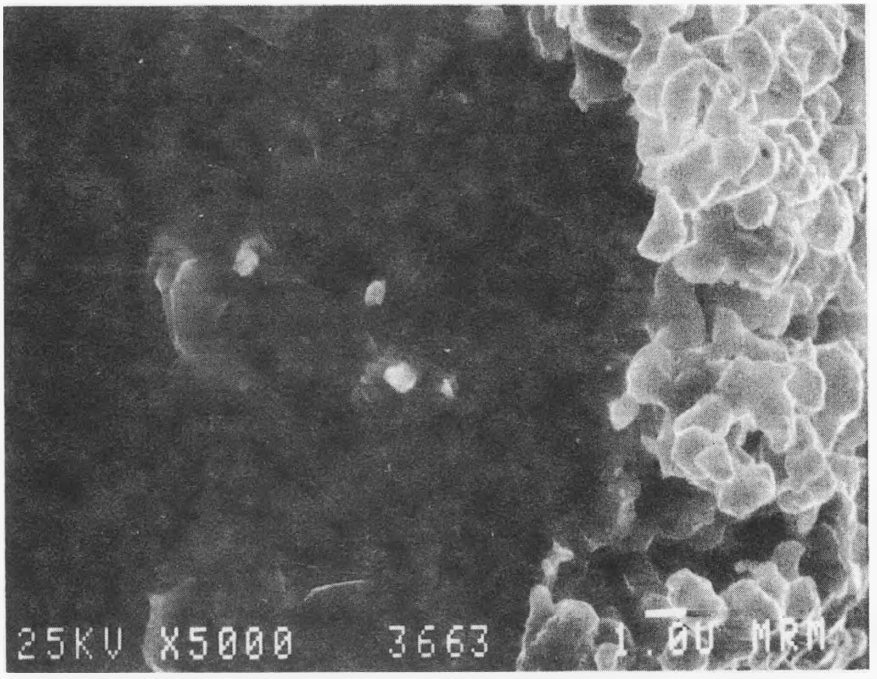



Figure 18. Higher magnification of unfluxed CdTe layer on CdS. (Area used for mapping and line scans.)

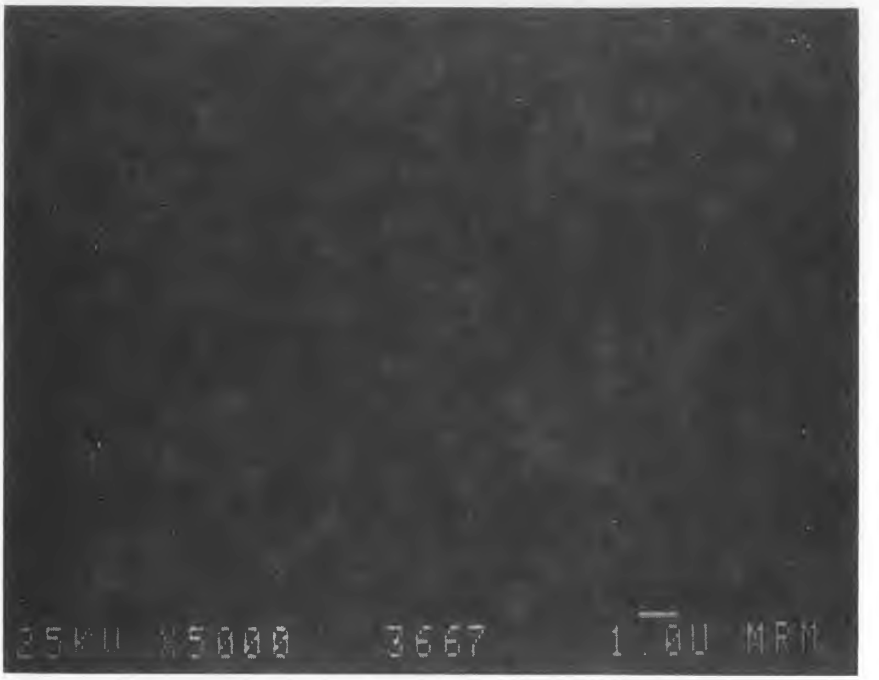



Figure 19. Sulfur map of unfluxed CdTe layer on CdS.

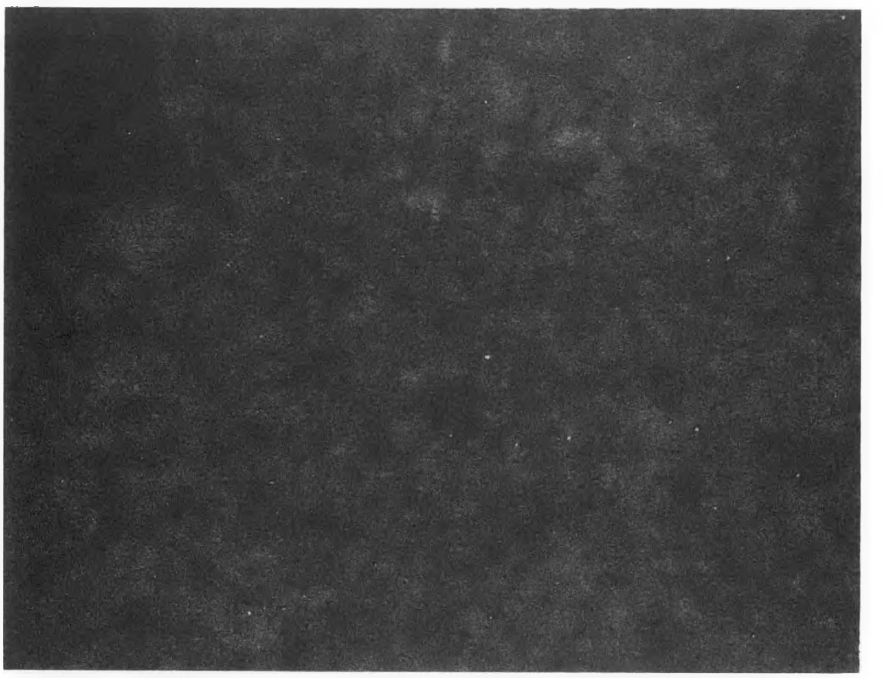


Figure 20. Tellurium map of unfluxed CdTe layer on CdS.

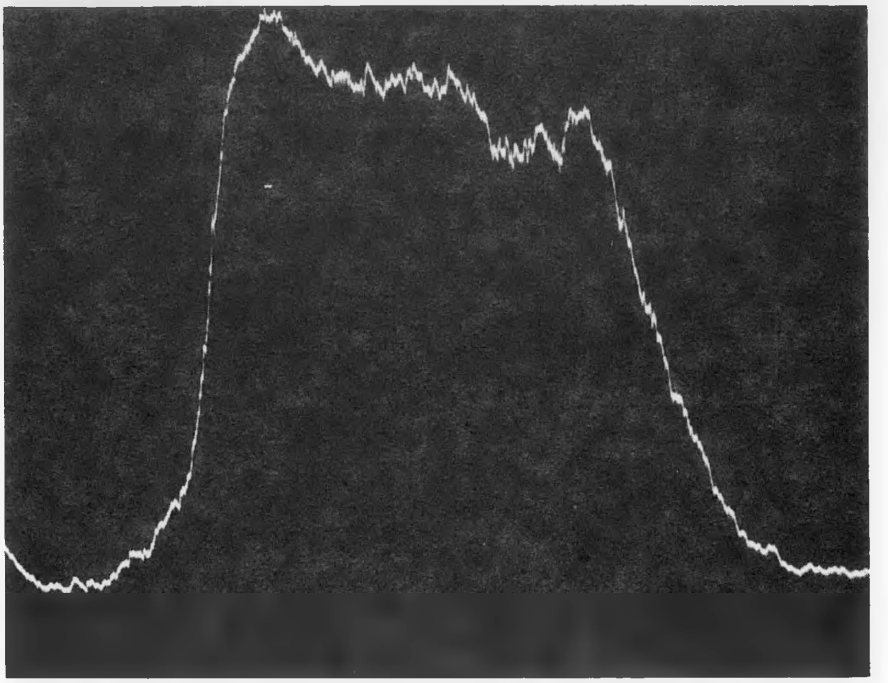


Figure 21. Sulfur line scan of unfluxed CdTe layer on CdS.

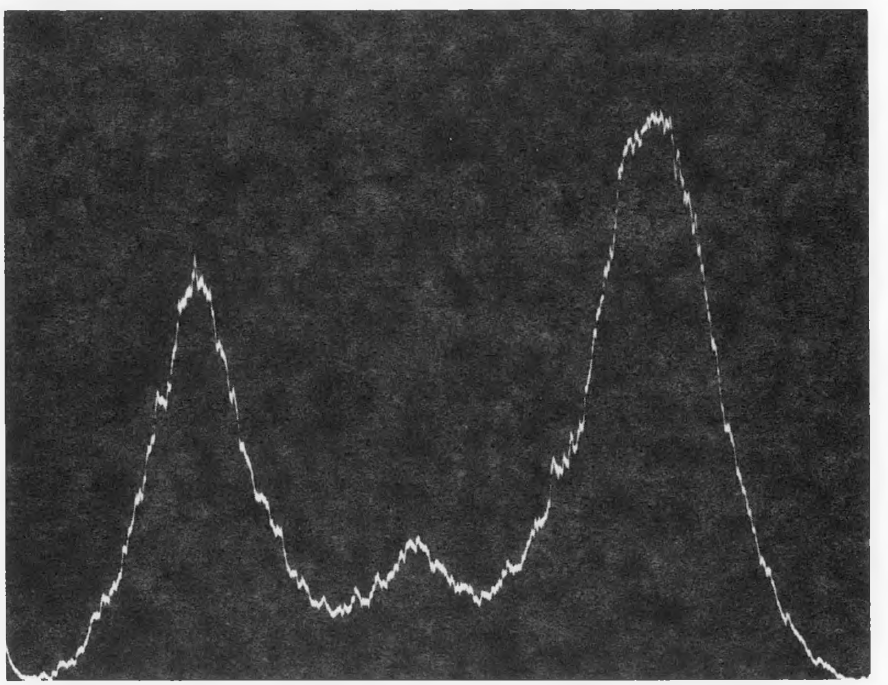


Figure 22. Tellurium line scan of unfluxed CdTe layer on CdS.

Most of the copper metallizations popped off as a single copper layer. The CdS where the metallization had been was discolored blue-black. The $V_{OC}$ of the completed cell was only 0.2 v and no further work on this approach was pursued.

4. Future Activities

Future activities will involve the completion of the modifications to the furnace; the systematic investigation of the firing of CdS and CdTe films as functions of firing temperature, time, and atmosphere; and the preparation of improved solar cells using the wet cuprous chloride approach.

Dr. Guy McDonald, Principal Investigator

Dr. G. Goodman, Project Manager

## Reference

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